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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : D21H 19/38, 19/42	A1	(11) International Publication Number: WO 98/20201 (43) International Publication Date: 14 May 1998 (14.05.98)
<p>(21) International Application Number: PCT/US97/20476</p> <p>(22) International Filing Date: 7 November 1997 (07.11.97)</p> <p>(30) Priority Data: 08/745,561 8 November 1996 (08.11.96) US</p> <p>(71) Applicant: S.D. WARREN COMPANY [US/US]; 89 Cumberland Street, Westbrook, ME 04092 (US).</p> <p>(72) Inventors: GUBRUD, Lisa, A.; 6 Joss Hill Road, Scarborough, ME 04074 (US). MASIA, Steven, L.; 114 East Bridge Street, Westbrook, ME 04092 (US). WAECKER, Thomas, A.; 7 Wainwright Drive, Cape Elizabeth, ME 04107 (US). YADETA, Baheru; 28 Windsor Pines Drive, Scarborough, ME 04074 (US).</p> <p>(74) Agent: O'REGAN, Briana, K.; S.D. Warren Technology Center, 89 Cumberland Street, P.O. Box 5000, Westbrook, ME 04098 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: COATED PRINTING PAPER AND METHOD OF MANUFACTURE</p> <p>(57) Abstract</p> <p>The invention provides a novel high gloss printing paper coated with a coating composition containing at least 80 parts precipitated calcium carbonate (PCC) and at least 5 parts hollow sphere plastic pigment, parts based on total weight of pigment. Preferably, the coating composition further contains titanium dioxide. A method of making a novel printing paper is also provided.</p>		

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Coated Printing Paper and Method of Manufacture

Technical Field

This invention relates to a coating composition for a novel high brightness, high gloss printing paper and to a method of manufacturing the novel high gloss printing paper.

Background of the Invention

The use of calcium carbonate, both natural ground and precipitated, to increase brightness in coating compositions for printing paper is well known in the art. In Europe, relatively high levels of calcium carbonate are routinely used in coating compositions. High levels of calcium carbonate, however, can lead to a variety of printing problems such as ink rub off, sheet marking and tail picking. Most coating compositions use 80% by weight or less in an effort to minimize these problems. Precipitated calcium carbonates are also used to reduce these printing problems because they are less abrasive than ground calcium carbonates. In addition, coatings containing high levels of calcium carbonate are generally restricted to matte, lightweight coated or rotogravure papers. In the United States, size press solutions are formulated for use with clay coatings and tend to worsen the printing problems when used with coatings containing high levels of calcium carbonate.

Hollow sphere plastic pigments are promoted by the manufacturers as useful for improving a wide variety of paper properties, such as paper gloss, print gloss, opacity and smoothness. They can also be used to increase bulk with reduced coat weights. The use of hollow sphere plastic pigments with high levels of calcium carbonate is not known.

It is an object of the invention to provide a printing paper that exhibits high brightness and high gloss coupled with minimized printing problems.

It is still another object of the invention to provide a method of manufacturing a high gloss printing paper.

Summary of the Invention

The invention provides a glossy printing paper comprising a paper substrate coated on at least one surface with a layer of coating composition comprising at least 80 parts precipitated calcium carbonate and at least 5 parts hollow sphere plastic pigment, parts based on 100 parts by weight of total pigment. Preferably the coating composition comprises 80 to 92 parts precipitated calcium carbonate and 6 to 12 parts hollow

sphere plastic pigment. The invention further provides a glossy printing paper wherein the layer of coating composition includes titanium dioxide pigment. The invention also provides a glossy printing paper wherein the layer of coating composition comprises less than 6 parts clay pigment. Preferably the dried coat weight of the coating composition is 8.9 to 16.3 g/m² (6 to 11 lb/3300 ft²), the hollow sphere plastic pigment is composed of an acrylic styrene copolymer with an average diameter of approximately 1.0 μm and a void volume of 55%, and the precipitated calcium carbonate has a median particle size of approximately 0.6 μm, a surface area of approximately 10 m²/g, and an aspect ratio of 2:1 to 3:1.

10 The invention further provides a method of making a glossy printing paper by applying a layer of coating composition to at least one surface of a paper substrate, the coating composition comprising at least 80 parts precipitated calcium carbonate and at least 5 parts hollow sphere plastic pigment, drying the coated substrate, and calendering the dried coated substrate. The method may also incorporate the other coating compositions described.

15 Other objects and advantages of the invention will be apparent to those skilled in the art from the following detailed description of preferred embodiments of the invention.

Description of Preferred Embodiments of the Invention

20 The glossy printing paper of the present invention is made by coating a paper substrate with a coating composition comprising at least 80 parts precipitated calcium carbonate (hereinafter PCC) and at least 5 parts hollow sphere plastic pigment, based on 100 parts by weight of total pigment.

The use in combination, in accordance with the invention, of at least 80 parts PCC and at least 5 parts hollow plastic pigment unexpectedly produced a printing paper with superior quality characteristics and with substantially improved printability. The combination provides improved coating-ink interaction, ink absorption, fountain solution absorption as well as a smooth uniform surface with high gloss and high brightness. The resulting printed image has high ink gloss, high ink uniformity and low microgloss.

25 The printing paper of the invention also exhibits excellent blister resistance. The improved runnability and printability of the paper is demonstrated in the substantially eliminated tail picking, marking and scuffing.

30 The coating composition of the invention comprises at least 80 parts by weight of PCC and at least 5 parts by weight of hollow sphere plastic pigment. Examples of

suitable PCC's include Albaglos L and Albaglos S, manufactured by Specialty Minerals, Inc. The PCC preferably has a median particle size of approximately 0.6 μm and a surface area of approximately 10 m^2/g . Most preferably, the PCC has an aspect ratio range of 2:1 to 3:1.

5 Suitable hollow sphere plastic pigments are available from Rohm & Haas Company, such as Ropaque HP-1055, OP-96 and HP-91. Preferably, the hollow sphere plastic pigment has an average particle diameter of approximately 1.0 μm and a void volume of approximately 55%. Most preferably, the hollow sphere plastic pigment is composed of an acrylic styrene copolymer.

10 The coating composition of the invention can further comprise less than 6 parts by weight clay. Those skilled in the art will know that the use of clay in coating compositions will decrease the brightness while improving other properties. In contrast, addition of clay in the present invention unexpectedly also decreased paper gloss and other final product attributes. The desired final product attributes will determine the
15 quantity of clay used in these coating formulations. Examples of suitable clays include Astra-Plus, available from ECCI, and Ansilex 93, available from Engelhard Corporation.

Preferably, the coating compositions of the invention further comprise natural or synthetic non-clay pigments, alone or in a mixture. Examples of suitable pigments include titanium dioxide, both anatase or rutile forms, aluminum hydroxide, satin white,
20 silica, organic pigments etc. It is to be understood that these pigments are listed by way of example and the pigments used for this invention are not limited to those listed. Most preferably, the non-clay pigment is titanium dioxide. An example of a suitable anatase titanium dioxide is TIONA-A2000, available from SCM Chemicals.

The preferred coating composition comprises 80 to 92 parts PCC and 6 to 12 parts
25 hollow sphere plastic pigment, parts based by weight of total pigment. For products requiring high opacity, the most preferred coating composition comprises 80 to 84 parts PCC, 6 to 12 parts hollow sphere plastic pigment and 9 to 12 parts titanium dioxide, parts based by weight of total pigment. Otherwise, the most preferred coating composition, balancing both final product quality and cost of production, comprises 85
30 to 92 parts PCC, 8 to 12 parts hollow sphere plastic pigment and less than 6 parts titanium dioxide, parts based by weight of total pigment.

The coating compositions of the invention are suitable for both sheet and web printing grades without modifications. Practitioners skilled in the art know that coating compositions generally must be modified for web grades because of the speeds and

high temperatures involved in web printing. Web printing papers tend to have lower moisture and more porous coating layers to reduce blistering during drying.

The coating composition of the invention further comprises a binder system, required for all paper coatings. Those skilled in the art will know that a binder system with starch will decrease brightness. It is preferred to use a latex binder system with
5 minimum quantities of starch. Latex binders that can be used in the invention include acrylic, styrene-butadiene, styrene-acrylate, urethane, acrylonitrile, carboxylated latices, etc. It is to be understood that these binders are listed by way of example and the binders used for this invention are not limited to those listed. Preferably, a blend of two
10 latex types, styrene-butadiene and styrene-acrylate, is used in the invention.

Practitioners skilled in the art know that coating formulations can include a variety of additives, such as dyes, fluorescent brighteners, dispersants, thickeners, lubricants, pH control agents, etc. The use of coating additives is determined by the final product attributes. It is to be understood that the invention is not limited to the additive
15 components listed.

The paper substrate of the invention is obtained by conventional papermaking techniques using any papermaking fibers. Preferably, the paper substrate will be woodfree. Those skilled in the art will understand that final product attributes and productivity factors will determine the particular mixture of papermaking fibers used. In
20 addition, the substrate is preferably sized with a starch precoat.

The coating composition of the invention can be applied by a variety of coating technologies. Examples of coating applications include bent blade, bevel blade, rod, short dwell, curtain coating, air knife etc. Practitioners skilled in the art will know that the invention is not limited to these techniques. In addition, those skilled in the art know that
25 modifications to the rheology of the coating compositions of the invention will be necessary depending on the coating technique employed.

The most preferred method of applying the coating composition of the invention is with a bent blade coater at a dried coat weight of 8.9 to 16.3 g/m^2 (6 to 11 lb/3300 ft^2) per side. The invention, however, includes paper products coated on only one side as
30 well as products double-coated on one or both sides. Practitioners skilled in the art will know that both the rheology and applied coat weights will vary depending on the final product attributes desired. In addition, the coating operation can be in a continuous in-line operation with the papermaking operation.

The invention includes the finishing step of calendering the dried coated paper. The method of calendering the paper of the invention is not restrictive. The paper can be calendered as a separate step, on a stand alone calender or supercalender, or can be calendered in a continuous in-line operation with the papermaking operation and/or the coating operation.

The following examples illustrate the invention and enable those skilled in the art to understand the invention. It shall be understood that the invention is not limited to the particular examples given below. Unless otherwise stated, all parts and percentages are by weight.

Table 1 lists the formulations and final product attributes of both invention and comparative examples. Examples 1 through 5 illustrate the present invention. Examples C1 through C3 are listed for comparison. All coating compositions were mixed in laboratory size batches, with a final coating solids of 58-60%. Bodystock with a basis weight of 71.0 g/m² (48 lb/3300 ft²) was coated on one side with each coating. The final coat weight was approximately 14.8 g/m² (10 lb/3300 ft²). The coated and dried samples were calendered in a laboratory calender, through one nip at high temperature and pressure. The tests were performed after the samples had conditioned for 24 hours in a constant humidity of 50%.

Table 1

	1	2	3	4	5	C1	C2	C3
Formulations:								
PCC	81	88	86	88	90	100	96.5	0
Hollow sphere plastic pigment	8	6	8	8	6	0	3.5	0
TiO ₂	11	6	6	4	0	0	0	0
Clay	0	0	0	0	4	0	0	75
Ground Calcium Carbonate	0	0	0	0	0	0	0	25
Properties:								
Brightness	92.8	94.0	93.8	92.0	91.3	93.5	94.4	86.3
75° Paper Gloss	80.7	76.0	81.0	81.0	73.1	50.0	50.0	81.1
20° Ink Gloss	66.0	69.0	68.5	73.0	57.3	30.4	28.0	60.5
Microgloss	273	272	270	320	400	189	230	505

Microgloss is a measure of point to point variation in gloss, which relates to image quality. It is measured using a 1.5 mm microgloss head in the Tobias Mottle tester. The lower the value, the more uniform the gloss of the surface.

5 The embodiments of the invention illustrated by the examples balance the desired final product attributes of high brightness, high paper gloss, high ink gloss and low microgloss.

10 While the preferred forms of the invention have been described and illustrated in the examples, variations will be apparent to those skilled in the art. The invention is not limited to these embodiments and modifications may be made without departing from the spirit of the invention or the scope of the appended claims.

It is claimed:

Claims

1. A glossy printing paper with improved printability comprising a paper substrate coated on at least one surface with a top layer of coating composition comprising at least 80 parts precipitated calcium carbonate and at least 5 parts hollow sphere plastic pigment, parts based on 100 parts by weight of total pigment.
2. A glossy printing paper according to claim 1 wherein the coating composition comprises 80 to 92 parts precipitated calcium carbonate and 6 to 12 parts hollow sphere plastic pigment, parts based on 100 parts by weight of total pigment.
3. A glossy printing paper according to claims 1 or 2 wherein the coating composition further comprises other natural or synthetic non-clay pigments.
4. A glossy printing paper according to claim 3 wherein at least one of the other natural or synthetic non-clay pigments is titanium dioxide.
5. A glossy printing paper according to claim 4 wherein the coating composition comprises 80 to 84 parts precipitated calcium carbonate, 6 to 12 parts hollow sphere plastic pigment and 9 to 12 parts titanium dioxide, parts based on 100 parts by weight of total pigment.
6. A glossy printing paper according to claim 4 wherein the coating composition comprises 85 to 92 parts precipitated calcium carbonate, 8 to 12 parts hollow sphere plastic pigment and less than 6 parts titanium dioxide, parts based on 100 parts by weight of total pigment.
7. A glossy printing paper according to claims 1 or 2 wherein the dried coat weight of said layer of coating composition is 6 to 11 lb/3300 ft².
8. A glossy printing paper according to claims 1 or 2 wherein the hollow sphere plastic pigment has an average diameter of approximately 1.0 μm and a void volume of approximately 55%.
9. A glossy printing paper according to claims 1 or 2 wherein the hollow sphere plastic pigment is composed of an acrylic styrene copolymer.

10. A glossy printing paper according to claims 1 or 2 wherein the precipitated calcium carbonate has a median particle size of approximately $0.6\ \mu\text{m}$ and a surface area of approximately $10\ \text{m}^2/\text{g}$.
- 5 11. A glossy printing paper according to claims 1 or 2 wherein the precipitated calcium carbonate has an aspect ratio range of 2:1 to 3:1.
12. A glossy printing paper with improved printability comprising a paper substrate coated on at least one surface with a top layer of coating composition comprising at least 80 parts precipitated calcium carbonate, at least 5 parts hollow sphere plastic pigment and less than 6 parts clay, parts based on 100 parts by weight of total pigment.
- 10 13. A glossy printing paper according to claim 12 wherein the coating composition comprises 80 to 92 parts precipitated calcium carbonate and 6 to 12 parts hollow sphere plastic pigment, parts based on 100 parts by weight of total pigment.
- 15 14. A glossy printing paper according to claims 12 or 13 wherein the coating composition further comprises other natural or synthetic non-clay pigments.
15. A glossy printing paper according to claim 14 wherein at least one of the other natural or synthetic non-clay pigments is titanium dioxide.
- 20 16. A glossy printing paper according to claims 12 or 13 wherein the dried coat weight of said layer of coating composition is 6 to $11\ \text{lb}/3300\ \text{ft}^2$.
17. A glossy printing paper according to claims 12 or 13 wherein the hollow sphere plastic pigment has an average diameter of approximately $1.0\ \mu\text{m}$ and a void volume of approximately 55%.
- 25 18. A glossy printing paper according to claims 12 or 13 wherein the hollow sphere plastic pigment is composed of an acrylic styrene copolymer.
19. A glossy printing paper according to claims 12 or 13 wherein the precipitated calcium carbonate has a median particle size of approximately $0.6\ \mu\text{m}$ and a surface area of approximately $10\ \text{m}^2/\text{g}$.
- 30 20. A glossy printing paper according to claims 12 or 13 wherein the precipitated calcium carbonate has an aspect ratio range of 2:1 to 3:1.

21. A method of making a glossy printing paper with improved printability by
- 5 a. applying a top layer of coating composition to at least one surface of a paper substrate, the coating composition comprising at least 80 parts precipitated calcium carbonate and at least 5 parts hollow sphere plastic pigment, parts based on 100 parts by weight of total pigment,
- b. drying the coated substrate, and
- c. calendering the dried coated substrate.
22. A method of making a glossy printing paper according to claim 21 wherein the coating composition comprises 80 to 92 parts precipitated calcium carbonate
- 10 and 6 to 12 parts hollow sphere plastic pigment, parts based on 100 parts by weight of total pigment particles.
23. A method of making a glossy printing paper according to claims 21 or 22 wherein the coating composition further comprises other natural or synthetic non-clay pigments.
- 15 24. A method of making a glossy printing paper according to claim 23 wherein at least one of the other natural or synthetic non-clay pigments is titanium dioxide.
25. A method of making a glossy printing paper according to claim 24 wherein the coating composition comprises 80 to 84 parts precipitated calcium carbonate, 6 to 12 parts hollow sphere plastic pigment and 9 to 12 parts titanium dioxide,
- 20 parts based on 100 parts by weight of total pigment.
26. A method of making a glossy printing paper according to claim 24 wherein the coating composition comprises 85 to 92 parts precipitated calcium carbonate, 8 to 12 parts hollow sphere plastic pigment and less than 6 parts titanium dioxide, parts based on 100 parts by weight of total pigment.
- 25 27. A method of making a glossy printing paper with improved printability by
- a. applying a top layer of coating composition to at least one surface of a paper substrate, the coating composition comprising at least 80 parts precipitated calcium carbonate, at least 5 parts hollow sphere plastic pigment and less than 6 parts clay, parts based on 100 parts by weight of total pigment,
- 30 b. drying the coated substrate, and
- c. calendering the dried coated substrate.

28. A method of making a glossy printing paper according to claim 27 wherein the coating composition comprises 80 to 92 parts precipitated calcium carbonate and 6 to 12 parts hollow sphere plastic pigment, parts based on 100 parts by weight of total pigment.
- 5 29. A method of making a glossy printing paper according to claims 27 or 28 wherein the coating composition further comprises other natural or synthetic non-clay pigments.
30. A method of making a glossy printing paper according to claim 29 wherein at least one of the other natural or synthetic non-clay pigments is titanium dioxide.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/20476

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 021H19/38 021H19/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 021H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE 24 53 910 A (RHONE PROGIL) 28 May 1975 see page 3, paragraph 4 - page 4, paragraph 4; claims; example 13 ---	1,2,7, 12,13, 16,21, 22,27,28
Y	US 3 931 061 A (KOHNE JR HARRY F ET AL) 6 January 1976 see the whole document ---	1,2,7, 12,13, 16,21, 22,27,28
A,P	US 5 677 043 A (HULTMAN JACK D ET AL) 14 October 1997 ---	
A	FR 2 009 372 A (DOW CHEMICAL CO) 6 February 1970 ---	
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

3 March 1998

Date of mailing of the international search report

11/03/1998

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 264 742 A (GOLDEN RONALD ET AL) 28 April 1981 ---	
A	WO 94 04603 A (DOW CHEMICAL CO ;LEE DOLK (US); MULDER MICHAEL R (US); NICHOLSON) 3 March 1994 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/20476

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 2453910 A	28-05-75	FR 2271333 A FR 2262717 A FR 2286916 A AT 347237 B BE 822238 A BR 7409577 A CH 592777 A DK 592874 A, B, GB 1463340 A JP 50080328 A JP 57002840 B NL 7414875 A SE 7414266 A US 4010307 A	12-12-75 26-09-75 30-04-76 11-12-78 14-05-75 25-05-76 15-11-77 14-07-75 02-02-77 30-06-75 19-01-82 20-05-75 16-05-75 01-03-77
US 3931061 A	06-01-76	NONE	
US 5677043 A	14-10-97	AU 1581897 A WO 9728006 A	22-08-97 07-08-97
FR 2009372 A	06-02-70	BE 733548 A DE 1926853 A GB 1229503 A NL 6908016 A, B, SE 362912 B US 3853579 A US 3779800 A	24-11-69 04-12-69 21-04-71 01-12-69 27-12-73 10-12-74 18-12-73
US 4264742 A	28-04-81	CA 1140759 A	08-02-83
WO 9404603 A	03-03-94	CA 2140035 A AU 666332 B AU 2506692 A BR 9207160 A DE 69219904 D DE 69219904 T EP 0656033 A FI 950733 A JP 8500621 T US 5521253 A	03-03-94 08-02-96 15-03-94 31-10-95 26-06-97 11-12-97 07-06-95 17-02-95 23-01-96 28-05-96